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Parameterization of the Potential Energy Surface of the Double Proton Transfer in Porphyrins

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We present a fast and precise generator of the potential energy surface (PES) for the double proton transfer occurring in free-base porphyrin. We propose novel analytical formulae of the PES along with their parameterizations to describe correlated motions of the protons.

1 Introduction

Double proton transfer processes (DPTs) are commonly observed, from small systems to large ones, including proteins. For a better understanding of DPTs and coupled, correlated atomic motions, we plan to use quantum-classical molecular dynamics (QCMD) simulations. The main problem in the QCMD simulations is the lack of reliable and fast PES generators for the atomic motions. Based on effective quantum-classical models^{1,2} and their numerical implementations, we decided to construct PES for model molecular systems with DPTs. Drawing experience from our previous research on DPTP in formic acid dimer (a system with two hydrogen bonds), we focused our research on larger and experimentally well-studied molecules with the intramolecular proton transfer: porphyrin and porphycene. Free-base porphyrin and porphycene are built of four pyrrole rings connected by carbon bridges and have two hydrogen atoms (protons) in the inner part of the skeleton. The two inner protons migrate in the molecular scaffold containing four nitrogen atoms. The double proton transfer could - in principle - proceed either along a synchronous pathway or *via* a two-step mechanism involving a metastable *cis* intermediate. All the stationary states presented in Fig. 1. were optimized using GAUSSIAN 03³ with

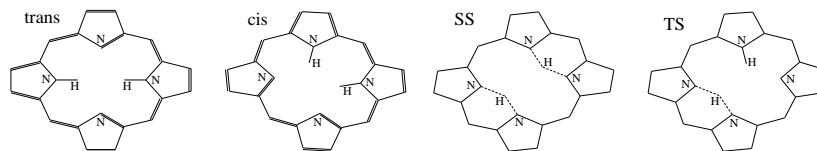


Figure 1. The stationary structural states of the porphyrin molecule obtained with the DFT/B3LYP method.

the spin-restricted B3LYP density functional method (DFT) and the 6-31G(d,p) basis set.

The obtained energy values are presented in Tab. 1, they are in good agreement with the B3LYP/TZ2P values given by Baker *et al.*⁴.

structure	energy (V^G)	energy ⁴	structure	energy (V^G)	energy ⁴
trans (D_{2h})	0.0	0.0	cis (C_{2v})	34.3	34.8
TS (C_s)	64.0	67.8	SS (D_{2h})	94.2	102.2

Table 1. Relative energies for the stationary states of the porphyrin PES (energies are given in [kJ/mol], the *trans* porphyrin is taken as the reference state).

2 Potential Energy Functions

Our aim is to construct a PES generator for the motions of the two inner protons and vibrations of the molecular skeleton, occurring in the ground Born-Oppenheimer state. Such a generator can be parametrized based on the *ab initio* or DFT calculations for the energies and the geometries of the stationary states (including the minima and the saddle points of the PES), and the corresponding Hessians, as well as on the PES scans for proton motions inside the molecular scaffold. Several models are considered; in one of them, the PES for the protons and for the skeleton is obtained with the Approximate Valence Bond (AVB) method¹ as the lowest eigenstate of the AVB Hamiltonian; in two other approaches, the PES for the molecular skeleton is described by a classical force field or by an average harmonic potential, and a more rigorous analytical representation of the PES for the proton motions is used, allowing for better approximation of the energy scans obtained with GAUSSIAN 03.

3 Mechanical PES Model

The following analytical formulae are used to describe the PES for the inner protons:

$$\begin{aligned}
 V_M := & \sum_H \left(\sum_N V_{NH} + \sum_C V_{CH} + \sum_{pairs NC} V_{HNC} + \sum_{pairs N} V_{NHN} \right) \\
 & + V_{HH} + \sum_N V_{HNH} + V_{const}(R_{skeleton}),
 \end{aligned}$$

where the first sum runs over the two protons and includes the following terms for each proton:

- two-body interactions with C and N atoms described by the Morse function for the bond length, CH and NH,

$$V_{CH} := P_{L1}(\exp(-P_{N1}r_{CH}) + P_{N2} \exp(-2P_{N1}r_{CH})),$$

$$V_{NH} := P_{L2}(\exp(-P_{N3}r_{NH}) + P_{N4} \exp(-2P_{N3}r_{NH})),$$

- three-body interactions with N and C atoms, ensuring proper angles between the NC and NH bonds,

$$V_{HNC} := P_{L3} \exp(-P_{N5} r_{NH}^2) \left(\frac{\vec{r}_{NC} \cdot \vec{r}_{NH}}{|\vec{r}_{NC}| |\vec{r}_{NH}|} + P_{N6} \right)^2,$$

- three-body interactions with pairs of N atoms (computed for each pair),

$$V_{NHN} := P_{L4} \exp(-P_{N7} r_{N1H}) \exp(-P_{N7} r_{N2H}).$$

The other terms are:

- a repulsive HH interaction,

$$V_{HH} := \frac{P_{L5} + P_{L6} \exp(-P_{N8} r_{HH}^2)}{r_{HH}},$$

- a three-body interaction between the two protons and a nitrogen atom (computed for each nitrogen),

$$V_{HNN} := P_{L7} \exp(-P_{N9} r_{NH1}) \exp(-P_{N9} r_{NH2}).$$

3.1 Fitting the Parameters

The mechanical PES model contains a set of parameters: $\{P_{Li}\}_{i=1}^7, \{P_{Ni}\}_{i=1}^9$, which have to be optimized in order to fit the model to the DFT results. The optimization is based on minimization of the root mean square deviation (RMSD) function:

$$RMSD := \sqrt{\frac{\sum_{\{geom\}} \left(\sum_{\{map\}} \mathcal{I}(V^G) (V_M - V^G)^2 \right)}{\sum_{\{geom\}} \left(\sum_{\{map\}} \mathcal{I}(V^G) \right)}},$$

where

$$\mathcal{I} = \begin{cases} 1 & \text{if } V^G \leq V^S \\ \exp(-V^G/V^S) & \text{if } V^G > V^S \end{cases},$$

and $\{map\}$ represents the set of positions of the protons, used to scan the PES at a fixed geometry of the skeleton, $\{geom\}$ represents the set of all the geometries of the skeleton (minima and transition states) for which the scans have been performed, V^S is an energy cutoff (e.g. $V^S=100$ kJ/mol for porphyrin). It should be emphasized that optimization is carried out simultaneously for all geometries that represent stationary states of the molecule.

4 Results

The mechanical PES model was fitted to the DFT calculations with a satisfactory accuracy. In the most important, low energy regions, up to 100 kJ/mol, the discrepancy between the model and the DFT results does not exceed 8 kJ/mol. In order to visualize the results of the parameterization, the protonic scans for the porphyrin molecule in the *trans* minimum state are presented in Fig 2. From the left to the right are shown: the reference PES scans obtained with GAUSSIAN 03 by moving the right inner proton in the plane of the

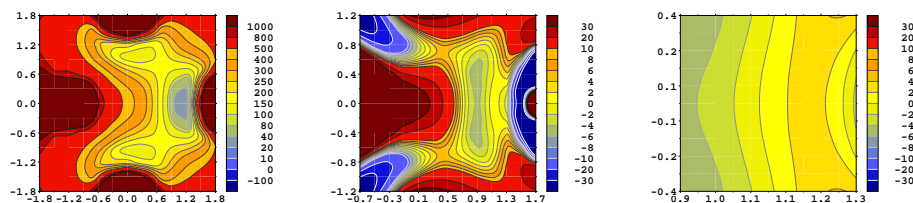


Figure 2. An *ab initio* scan of the PES (left), and the differential energy maps (middle and right) - for details, see the text.

molecule (x, y) in the region $(x, y) \in (-1.8; 1.8)$, while all other atoms were fixed in space; the differences between the protonic scans obtained with GAUSSIAN 03 and with the analytical model in the region limited to $x \in (-0.7; 1.7)$, $y \in (-1.2; 1.2)$; and the right one to $x \in (0.9; 1.3)$, $y \in (-0.4; 0.4)$. Note that the (x, y) coordinates of the nitrogen atoms are: $(0.00; 2.03)$, $(0.00; -2.03)$, $(2.12; 0.00)$, $(-2.12; 0.00)$. The NH bond lengths in the local minima, the transition state and the saddle point of GAUSSIAN 03 as well as the parametrized PES (V_M) are summarized in Tab. 2. In the case of the transition states, the distances between the proton and the two closest nitrogen atoms are given.

structure	R_1	R_1^G	R_2	R_2^G
trans (D_{2h})	1.0074	1.0145	1.0074	1.0145
cis (C_{2v})	1.0204	1.0277	1.0204	1.0277
TS (C_s)	1.0225	1.0273	1.9020 , 1.2982	1.8772, 1.2833
SS (D_{2h})	1.2927 , 1.2927	1.2943, 1.2943	1.2927 , 1.2927	1.2943, 1.2943

Table 2. NH bond lengths (given in Å) of the stationary states in porphyrin.

Acknowledgments

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